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(57) Abstract

High gloss finishes cured by electron beam without the need for a fully inert atmosphere are attained by providing a coating composition having a non-volatile photoinitiator and a flow control agent. In the method of producing the high gloss finishes, the coating is first exposed to electron beam in air or a partially inert atmosphere, then exposed to ultraviolet radiation in an essentially inert atmosphere.

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COMPOSITIONS AND METHODS FOR PRODUCING HIGH GLOSS RADIATION CURABLE COATINGS

BACKGROUND OF THE INVENTION

Radiation curable coatings are highly desirable because they can be cured without the need to evaporate substantial amounts of solvent. Therefore, curing can be accomplished rapidly and with less release of volatile organic compounds into the atmosphere. Also, radiation curing can be carried out at relatively low temperatures, thereby lending itself to use with temperature sensitive substrates such as wood and plastic. The use of electron beam radiation is particularly favored for curing thick coatings and coatings that are heavily pigmented.

It is known to cure certain coating compositions to a glossy finish using electron beam radiation to initiate the crosslinking reactions that result in a cured film. The curing of typical radiation curable coating compositions is inhibited by the presence of oxygen, so it is conventional to provide a substantially inert atmosphere (e.g., less than 200 parts per million oxygen) in the electron beam exposure apparatus. It can be costly to maintain the required degree of inertness accurately and constantly. Slight variations in the oxygen concentration can lead to uneven coating appearance with conventional methods and compositions. It would be desirable to reduce the sensitivity of an electron beam curing system to oxygen when producing glossy coatings.

It is known to add accelerator compounds (e.g., tertiary amino compounds) to coating compositions to at least partially overcome the inhibition of curing due to oxygen, thereby increasing the amount of oxygen that can be permitted in the radiation curing chamber. Although the accelerators provide processing advantages, they generally have deleterious effects on the coating, such as yellowing and/or surface roughness. The accelerators can sometimes also have a negative effect on the ease of applying the coating composition onto the substrate.

Multi-step radiation curing processes, which may include a combination of electron beam and ultraviolet radiation, have been employed to produce low gloss coatings. In these prior art processes oxygen (air) was intentionally present during the first radiation curing step to initially inhibit polymerization at surface portions of the coating, and curing of the coating was completed in a subsequent step in an inert atmosphere. Shrinkage of underlying layers during the first step caused pigment particles to be driven into the surface portions, whereby the surface contained a larger amount of pigment than the body of the film which reduced the gloss of the film without sacrificing film strength or rheology properties of the coating composition. U.S. Patent Nos. 3,918,393 (Hahn) and 4,048,036 (Prucnal) illustrate this approach. Multi-step radiation curing techniques have also been proposed for producing textured finishes in U.S. Patent Nos. 4,421,784 (Troue), 3,840,448 (Osborne et al.), and 4,411,931 (Duong) wherein surface wrinkling of the coating is induced by the staged curing process. Those of skill in the art would have considered two stage radiation cure processes inappropriate for producing high gloss finishes.

SUMMARY OF THE INVENTION

By the present invention it has been found that electron beam radiation can be employed to yield high gloss finishes from certain coating compositions without requiring the fully inert (i.e. less than 200 parts per million oxygen) required by prior art processes. The process uses a two step curing process and selected coating compositions. Achieving high gloss finishes from a two step process is surprising in view of the fact that multi-step processes have previously been used for producing low gloss finishes. Furthermore, the substantial lessening of the requirement for a fully inert atmosphere during the electron beam radiation step is highly advantageous for the sake of reducing costs associated with atmosphere control.

The first step of the process of the present invention

involves irradiation with an electron beam, followed by a subsequent step of exposure to ultraviolet radiation. The electron beam step may take place in air or in a partially inert atmosphere including at least 2 percent oxygen by volume, whereby the surface of the coating remains wet or uncured. The ultraviolet radiation step takes place in a substantially inert atmosphere (e.g., less than 1000 parts per million oxygen) whereby curing of the coating is substantially completed. Although an inert atmosphere is required in the ultraviolet step, it may be noted that the conditions need not be controlled as rigorously as in prior art electron beam processes.

The coating compositions of the present invention are characterized by: a resin binder curable by radiation exposure in the presence of at least one photoinitiator compound, a relatively non-volatile photoinitiator compound, and a flow control agent such as a siloxane.

DETAILED DESCRIPTION

The binder or vehicle in the coating composition of the present invention comprises at least one resin (monomer, oligomer, or polymer) which is curable by exposure to radiation in the presence of one or more of the photoinitiators disclosed herein. Binder may constitute 10 to 99, preferably 50 to 99, percent by weight of the total coating composition. Many such resins are known in the art and may be used in the present invention. The resins suitable for use in the present invention are characterized by inhibition of curing by the presence of oxygen (such as in air). Oxygen inhibition permits maintaining an at least partially uncured surface layer during the initial curing step with the electron beam. A particular category of useful radiation curable compounds are characterized by a plurality of acrylyloxy groups and the ability to free radically addition polymerize upon being initiated by a photoinitiator or ionizing radiation. Unless otherwise indicated either directly or by context, acrylic unsaturation is used in its broad sense to mean the unsaturation provided by unsubstituted acrylyl groups or

a-substituted acrylyl groups such as methacrylyl, ethacrylyl and a-chloroacrylyl. Examples of these compounds are the diacrylates and dimethacrylates of ethylene glycol, 1,3-propanediol, propylene glycol, 2,3-butanediol, 1,4-butanediol, 2-ethylbutane-1,4-diol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 2,10-decanediol, 1,4-cyclohexanediol, 1,4-dimethylolcyclohexane, 2,2-diethylpropane-1,3-diol, 2,2-dimethylpropane-1,3-diol, 3-methylpentane-1,4-diol, 2,2-diethylbutane-1,3-diol, 4,5-nonanediol, diethylene glycol, triethylene glycol, propylene glycol, neopentyl glycol, 5,5-dimethyl-3,7-dioxanonane-1,9-diol, 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate; the triacrylates and diacrylates of glycerol, 1,1,1-trimethylolpropane and trimethylolethane; and the tetraacrylates, triacrylates, and diacrylates of pentaerythritol and erythritol. The acrylyloxy groups in each of the molecules are usually the same, but they may be different as exemplified by the compound 2,2-dimethyl-1-acrylyloxy-3-methacrylyloxypropane.

Further examples of satisfactory polyacrylyloxy compounds that may be included in the radiation curable resin include polyacrylyloxy functional polyesters, polamides, polyacrylates, polyethers, polycarbonates or polyurethanes as well as polyacrylyloxy functional compounds of mixed functionality such as polyacrylyloxy functional poly(ester-urethanes), poly(ester-amides) and poly(ether-urethanes). Mixtures of compounds having a plurality of acrylyloxy groups may be used, if desired.

The amount of polymerizable compound having a plurality of acrylyloxy groups present in the coating composition is subject to wide variation. The compound is ordinarily present in an amount in the range of from about 10 to 99 percent by weight based on the weight of the binder of the coating composition. An amount in the range of from about 20 to 97 percent is typical. From about 30 to 95 percent by weight of the binder is preferred.

Monomers having monoacrylic functionality which crosslinks

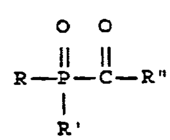
with the compound having polyacrylyloxy functionality may optionally be present in the coating composition. Examples of monoacrylic functional monomers which may be used are methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, hexyl ethyl acrylate, hexyl butyl acrylate, 2-ethyl hydroxy acrylate, octyl acrylate, hydroxy ethyl acrylate, hydroxy butyl acrylate, caprolactone-hydroxyl alkyl acrylate reaction products, and 2-ethyl hydroxy acrylate. The preferred monoacrylic functional monomers are liquid compounds miscible with the polyacrylyloxy compound. A benefit from the use of one or more monoacrylic functional monomers is that the monoacrylic functional monomer may act as a reactive solvent for the polyacrylyloxy functional compound, thereby providing coating compositions having a satisfactory low viscosity while using relatively small amounts or no volatile, nonreactive solvent.

The monoacrylic functional monomer, or mixtures of monoacrylic functional monomers, may be employed over a broad range, although none is required. The amount of such monomer when used should be sufficient to provide a liquid, flowable, interpolymerizable mixture. When used, the monomer will ordinarily be present in the coating composition in the range of from about 0 to about 80 percent by weight of the binder of the coating composition. Typically, the monoacrylic functional monomer will be present in the range of from about 0 to about 30 percent by weight of the binder. Other monovalent functional monomers may be employed as known in the radiation curing art, including N-vinyl-2-pyrolidone, vinyl neodecanoate, and other ethylenic unsaturated monomers known to be suitable for radiation curable coatings.

The present invention involves a coating composition containing a photoinitiator. Photoinitiators absorb radiation and thereby obtain energy to form free radicals that initiate polymerization of the binder resin. The photoinitiator in the present invention is one which forms free radicals upon exposure to actinic radiation, viz., ultraviolet light. In order to produce the high gloss finishes of the present invention, it has been found

desirable to select photoinitiators that are non-volatile, which is generally related to the molecular weight of the photoinitiator or its ability to copolymerize with other constituents of the composition. Therefore, for the purpose of the present invention, the non-volatile photoinitiator is generally characterized by a molecular weight of at least 260. Preferred examples had molecular weights greater than 300, with the best results achieved with molecular weights greater than 1000. Alternatively, the non-volatile photoinitiator may be characterized as having a copolymerizable functionality such as an acrylate group, even though its molecular weight may be slightly lower than 260. An example of a polymerizable photoinitiator is 4-(2-acryloxyloxyethoxy) phenyl-(2-hydroxyl-2-propyl) ketone.

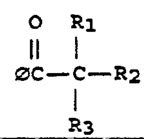
One suitable class of photoinitiators from which the photoinitiators of the present invention may be selected are the acylphosphine oxides. These photoinitiators cleave when exposed to ultraviolet radiation, and their residues in the cured film advantageously do not impart unwanted coloration to the film. Acylphosphine oxide photoinitiators are disclosed in U.S. Patent Nos. 3,668,093 and 4,447,520 and may be characterized by the formula:



where R and R' may be linear or branched 1 to 6 carbon alkyl, cyclohexyl, cyclopentyl, aryl, halogen-, alkyl-, or alkoxy-substituted aryl, or 5- or 6-membered S- or N-heterocyclic groups; R' may additionally be 1 to 6 carbon alkoxy, aryloxy, or arylalkoxy, or forms a ring with R; R" is linear or branched 2 to 18 carbon alkyl, a 3 to 12 carbon cycloaliphatic group, an alkyl- or (thio)alkoxy-substituted phenyl or naphthyl group, or a 5- or 6-membered S- or N-heterocyclic group which can contain other functional groups, or an -X-CO-P(=O)R-R' group (where X is a

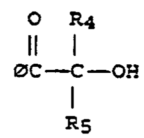
phenylene or 2 to 6 carbon (cyclo)aliphatic divalent group. R, R', or R" may include unsaturation. A particular example of an acylphosphine oxide is 2,4,6-trimethyl benzoyl diphenyl phosphine oxide, which is sold under the name "Lucirin® TPO" by BASF Corporation. In selecting photoinitiators, one of skill in the art would consider it expedient to select compounds that are soluble and stabile in the particular composition.

There are many other photoinitiators which may be used in the coating compositions of the present invention. Another class of compounds useful as photoinitiators in the present invention are acetophenone derivatives meeting the definition of non-volatile set forth above. Many acetophenone derivatives are known as photoinitiators, a large number of which are disclosed in U.S. Patent No. 4,229,274 (Carlblom). Acetophenone derivative photoinitiators may be generally characterized by the formula:



where R_1, R_2, and R_3 may, for example, include independently hydrogen, alkyl usually having from 1 to 6 carbon atoms (preferably 1 to 4 carbon atoms), alkoxy, cycloalkyl, or substituted or unsubstituted phenyl groups, and d is a phenyl group.

A particularly useful family of acetophenone derivatives has the following structure:



where R_4 and R_5 are alkyl groups having from 1 to 4 carbon atoms, and d is a phenyl group.

The amount of photoinitiator present in the coating composition is preferably at least 0.01 weight percent based on total solids content of the coating composition. Although larger amounts could be used, it is usually uneconomical to use more than 5 percent of the photoinitiator. Typically, the photoinitiator may be present in an amount of at least 0.1 percent, most often in the range of from 0.5 percent to 2 percent. Mixtures of more than one photoinitiator compound may be used.

The coating compositions of the present invention include a surfactant of the type that serves as a flow control agent or leveling agent. A large number of products are commercially available for this purpose, and many of them are siloxane or fluorocarbon compounds. The preferred class of flow control agents are siloxane compounds, examples of which are "BYK®-310, a polyester modified dimethylpolysiloxane " from Byk Chemie, Wallingford, Connecticut, and "Versaflow 102," a modified methyl siloxane from Shamrock Technologies, Inc., Newark, New Jersey. Examples of fluorocarbon flow control agents are the "Zonyl®" surfactants from DuPont and the "Fluororad®" surfactants, particularly "FC430," from 3M. The flow control agents for use in the present invention are characterized by the property of assisting leveling of the coatings of the present invention after application onto a substrate, without substantial interference with the application process itself. It is also desirable for the flow control agent to have relatively low volatility. The flow control agent may be present in the composition

in amounts ranging from 0.01 to 1.0 percent by weight based on total solids content of the composition.

Pigments may be included in the coating composition. Examples of opacifying pigments include titanium dioxide (rutile or anatase), zinc oxide, zirconium oxide, zinc sulfide and lithopone. Examples of coloring pigments include iron oxides, cadmium sulfide, carbon black, phthalocyanine blue, phthalocyanine green, indanthrone blue, ultramarine blue, chromium oxide, burnt umber, benzidine yellow, toluidine red, aluminum powder and aluminum flakes. Examples of extender pigments include silica, barytes, calcium carbonate, barium sulfate, talc, aluminum silicates, sodium aluminum silicates, potassium aluminum silicates and magnesium silicate. A single pigment may be used or mixtures of pigments may be employed. When the pigment is ultraviolet light absorbing, it should be used in amounts which do not preclude curing of the interior of the coating. The maximum amount is therefore related to the thickness of the coating to be cured. Thin coatings may tolerate more ultraviolet light absorbing pigment than thick coatings. When the pigment does not significantly absorb ultraviolet light, there is usually greater latitude in the amounts which may be employed. When pigment is used, it is generally present in an amount in the range of from about 0.1 to about 70 percent by weight of the coating composition. Often it is present in an amount in the range of from about 0.5 to about 50 percent. Usually it is present in an amount in the range of from about 1 to about 35 percent by weight of the coating composition. Dyes and tints may optionally be included in the coating composition as replacements for all or some of the pigment content.

Other optional ingredients are resinous pigment dispersants, viscosity control agents (e.g., cellulose acetate butyrate or resinous acrylics), plasticizers, or grinding vehicles such as non-reactive acrylics. There are many resinous additives which are commercially available which may be used for these purposes. These additives are used in the manner and in amounts known to the art, such as 0 to 20 weight percent of the total

composition.

Another ingredient which is often included in coating compositions of this type is a non-reactive, volatile organic solvent. However, in preferred embodiments of the present invention, no such non-reactive solvent need be included. In other embodiments of the invention, solvent may be present, but in lesser amounts than conventional. It is generally advantageous to minimize the amount of organic solvent, but if reduction of viscosity is desired for a particular application, the present invention does not preclude adding larger amounts of a non-reactive solvent or mixtures of several solvents. Examples of suitable non-reactive organic solvents are acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, secutyl alcohol, isobutyl alcohol, tert-butyl alcohol, amyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, cellosolve, ethyl cellosolve, cellosolve acetate, 2-ethylhexyl acetate, tetrahydrofuran, and aliphatic naphtha. When solvent of this type is used it is ordinarily present in the coating composition in the range of from about 0.1 to about 40 percent by weight of the vehicle of the coating composition. From about 0 to about 15 percent is typical. The preferred compositions are solvent-free.

The listing of optional ingredients discussed above is by no means exhaustive. Other ingredients may be employed in their customary amounts for their customary purposes so long as they do not seriously interfere with good coatings practice or the obtaining of cured coatings of high gloss.

The coating compositions of the invention are usually prepared by simply admixing the various ingredients. The compounds comprising the photocatalyst system may be premixed and then admixed with the other ingredients of the coating composition or they may be added separately. Although mixing is usually accomplished at room temperature, elevated temperatures are sometimes used. The maximum temperature which is usable depends upon the heat stability of the ingredients. Temperatures above about 200OF (93OC) are only rarely

employed.

The radiation curable coating compositions of the invention are generally used to form cured adherent coatings on substrates. The substrate is coated with the coating composition using substantially any technique known to the art. These include spraying, curtain coating, dipping, roller application, printing, brushing, drawing and extrusion. Wet, uncured coatings as applied to a substrate have thicknesses of at least 1.0 mil (0.025 millimeter), preferably at least 2.5 mils (0.06 millimeters), in order to achieve the low gloss effect of the present invention. Theoretically there is no upper limit for wet coating thickness, but in order to effect first stage curing of lower strata at practical radiation power levels, it is expedient to limit coating thickness to 5 to 8 mils (0.13 to 0.2 millimeters). Cured coatings of the ultraviolet light curable coating composition of the invention usually have thicknesses in the range of from 1 to 5 mils (0.025 to 0.13 millimeter). More often they have thicknesses in the range of from 2 to 4 mils (0.05 to 0.1 millimeter).

Substrates which may be coated with the compositions of this invention may vary widely in their properties. Organic substrates such as wood, fiberboard, particle board, composition board, paper, cardboard and various polymers such as polyesters, polyamides, cured phenolic resins, cured aminoplasts, acrylics, polyurethanes and rubber may be used. Inorganic substrates are exemplified by glass, quartz and ceramic materials. Many metallic substrates may be coated. Exemplary metallic substrates are iron, steel, stainless steel, copper, brass, bronze, aluminum, magnesium, titanium, nickel, chromium, zinc and alloys.

The method of curing the coating composition of the present invention involves a two step radiation exposure wherein the applied coating layer is cured in a subsurface portion in a first step by exposure to ionizing radiation (e.g., electron beam radiation or laser) in the presence of oxygen whereby curing at the surface is inhibited. In a subsequent step the curing is completed throughout

the remainder of the coating thickness by means of ultraviolet radiation in an at least partially inert atmosphere (i.e., less than 1000 ppm oxygen).

Suitable electron beam radiation for use in the first curing step may constitute a dose of 2 to 10 megarads, preferably 3 to 7 megarads, at 150 to 300 kiloelectron volts, preferably about 250 kiloelectron volts. Line speeds of 50 to 120 feet per minute (15 to 36 meters per minute) are suitable. The exposure in the first step is chosen so as to substantially cure the portion of the coating closest to the substrate. A portion of the coating thickness nearest to the surface will remain at least partially uncured due to oxygen inhibition. The atmosphere in the vicinity of the coating during the electron beam exposure should include at least 2 percent oxygen by volume.

Any suitable source which emits ultraviolet light, viz., electromagnetic radiation having a wavelength in the range of from about 180 to about 400 nanometers, may be used in the practice of the second curing step. Suitable sources are mercury arcs, carbon arcs, medium pressure mercury lamps, high pressure mercury lamps, swirl-flow plasma arc, ultraviolet light-emitting diodes and ultraviolet light emitting lasers. Particularly preferred are ultraviolet light emitting lamps of the medium or high pressure mercury vapor type. Such lamps usually have fused quartz envelopes to withstand the heat and transmit the ultraviolet radiation and are ordinarily in the form of long tubes having an electrode at either end.

The time of exposure to ultraviolet light and the intensity of the ultraviolet light to which the coating composition is exposed may vary greatly. For practical commercial line speeds, lamps rated at 200 watts per inch (7900 watts per meter) or greater are preferred. Generally the exposure to ultraviolet light should continue until either the film is thermoset throughout or at least cured to the point where subsequent reactions cause the film to become thermoset throughout. Exposure of the coating to ultraviolet

light may be accomplished in the presence of an inert atmosphere, viz., an atmosphere either containing no oxygen or only a concentration of oxygen which insignificantly inhibits polymerization of the coating surface (less than 1000 parts per million oxygen). Gases such as nitrogen, argon, carbon dioxide or mixtures thereof are typically the major components of inert atmospheres, although other unreactive gases may be used. Nitrogen is generally employed for this purpose.

Coatings produced in accordance with the present invention exhibit gloss and distinctness of image comparable to that of coatings produced with full inerting (less than 200 parts oxygen per million). Gloss may conveniently be determined by the Standard Method of Test for Specular Gloss, ASTM Designation D-523-67 (Reapproval 1971). Using a Gardner 60° glossmeter, the gloss of cured coatings of the present invention may exceed 70 percent reflected light, preferably greater than 80 percent, and with specific examples being in the range of 83 to 86 percent.

Another measure of the gloss of coatings is "distinctness of image" (D.O.I.). The particular distinctness of image test used to evaluate the present invention employs a technique specified by General Motors Standard Engineering Test: Distinctness of Image GM91013 Page Reference W-65.201. In this test, a light source (a Model GB11-8 Glowbox made by I2R Corporation) is used to project a series of successively smaller images of the letter "C" onto the coated surface from a fixed distance. The smaller the image that is

reflected, the higher the D.O.I. rating on a scale of 0 to 100. High gloss coatings generally exhibit D.O.I. ratings of at least 80, preferably at least 85. Coatings cured with full inerting during the electron beam exposure step may have D.O.I. ratings in the range of 90 to 100.

EXAMPLE 1

This example demonstrates a specific embodiment of the composition and method of the present invention.

Constituent	Percent by weight
Diacrylate resin[1]	92.5
Cellulose acetate butyrate resin	4.0
Lampblack pigment[2]	1.2
Dispersant[3]	1.2
Photoinitiator[4]	1.0
Flow control agent[5]	0.1

[1]Low viscosity polyester diacrylate "SR606A" from Sartomer Corporation, Exton, Pennsylvania, U.S.A.

[2]Grade #6 amorphous, acidic carbon black from General Carbon Company, Los Angles, California, U.S.A.

[3]"Sartomer 802" acrylic monomer with pigment dispersing characteristics from Sartomer Corporation, Exton, Pennsylvania, U.S.A.

[4]"Esacure KIP100F" photoinitiator comprising 70% oligo {2-hydroxy-2-methyl-1-[4-(methylvinyl)-phenyl] propanone} and 30%2-hydroxy-2-methyl-1-phenyl propan-1-one, from Sartomer Corporation, Exton, Pennsylvania, U.S.A. Molecular weight is reported to be 2000.

[5]"Versaflow 102" modified methyl siloxane from Shamrock Technologies, Inc., Newark, New Jersey.

A portion of the diacrylate together with the dispersant and the lampblack pigment were ground in a pigment mill with ceramic media. The grind was then flushed out of the mill with an additional portion of the diacrylate. The composition was then let down with the remainder of the diacrylate premixed with the cellulose acetate butyrate, the photoinitiator, and the siloxane flow control agent.

The composition above was applied at a wet film thickness of 2.5 mils (0.06 millimeters) with a curtain coater onto medium density fiberboard that has been filled, sealed, and sanded smooth.

The coated substrate was cured by at a line speed of 100 feet per minute (30.5 meters per minute), first with an electron beam manufactured by Energy Sciences, Inc., of Woburn, Massachusetts, USA, set at 250 kilovolts terminal voltage and 23 milliamperes beam current, yielding 5 megarads of energy, in an atmosphere containing 10% oxygen by volume. In a second curing step the coated substrate was subjected to ultraviolet exposure from four medium pressure mercury vapor lamps of 200 watts per inch (80 watts per centimeter) manufactured by Aetek International, Plainfield, Illincis, USA, at a line speed of 80 feet per minute (24 meters per minute) in a fully inerted atmosphere (nitrogen with less than 200 parts per million oxygen). A highly glossy finish was produced as reported in Table 1.

EXAMPLE 2

This example employs the same two stage curing process with electron beam and ultraviolet stages as used in Example 1, but uses a conventional radiation curable coating composition. Therefore, a polymeric surfactant was not included in the composition of this example. Also, a lower molecular weight photoinitiator was used ("Irgacure 651" from Ciba-Geigy Corp., Hawthorne, New York, having a molecular weight of 256). Substantially lower gloss was produced in this example as can be seen in Table 1.

EXAMPLE 3

This example employs the same prior art coating composition as in Example 2, but curing was carried out in a single stage process using only the electron beam described in Example 1. The electron beam stage was fully inerted. Even though curing was carried out in a fully inerted atmosphere, the results as reported in Table 1 were not as good as Example 1.

EXAMPLE 4

This example is the same as Example 4, with the exception that no photoinitiator was included in the coating composition in

view of the use of a single stage electron beam curing process. The results as reported in Table 1 are the same as Example 3, indicating that the presence of photoinitiator was not the cause of the inferior gloss of Example 3 relative to the present invention as represented by Example 1.

TABLE 1

	Gloss	D.O.I.
Example 1 (The invention)	85	90
Example 2 (Prior art composition)	70	50
Example 3 (Single stage)	85	80
Example 4 (Single stage)	85	80

The examples set forth above demonstrate that the particular composition of the present invention (Example 1), when cured by a two stage process that does not employ full inerting in the electron beam stage, can yield finishes having gloss subtantially superior to that attained by a typical prior art compositions cured by the same process (Example 2). That this result can be attained without the need to fully inert the electron beam stage is highly advantageous and surprising. Also surprising is finding that the gloss attained by Example 1 (the invention) is better even than that produced by a fully inerted electron beam (Examples 3 and 4).

The invention has been disclosed in connection with specific embodiments in order to provide the best mode of the invention, but it should be understood that other variations and modifications as would be known to those of skill in the art can be resorted to within the scope of the invention as defined by the claims which follow.

THE CLAIMS:

1. A radiation curable coating composition adapted to produce a high gloss film, comprising:

a resin binder curable by radiation exposure in the presence of at least one photoinitiator compound, the resin being selected from those whose curing by radiation exposure is substantially inhibited by the presence of oxygen;

a non-volatile photoinitiator; and

flow control agent.

2. The composition of claim 1 wherein the photoinitiator is characterized by a molecular weight of at least 260.

3. The composition of claim 1 wherein the photoinitiator is characterized by a molecular weight of at least 300.

4. The composition of claim 1 wherein the photoinitiator is characterized by a molecular weight of at least 1000.

5. The composition of claim 1 wherein the photoinitiator is characterized by a functional group copolymerizable with other polymerizable constituents of the composition.

6. The composition of claim 1 wherein the photoinitiator comprises a substituted acetophenone derivative.

7. The composition of claim 1 wherein the flow control agent is selected from the group consisting of silanes and fluorocarbons.

8. The composition of claim 7 wherein the flow control agent is a polysiloxane.

9. The composition of claim 1 comprising:

10-99 weight percent of the binder;

0.01-4 weight percent of the photoinitiator; and

0.01-1 weight percent of the flow control agent.

10. The composition of claim 1 wherein at least 10 percent by weight of the binder is polyacrylyloxy compound.

11. The composition of claim 1 wherein at least 30 percent by weight of the binder is polyacrylyloxy compound.

12. A method of producing a high gloss, radiation cured coating comprising:

applying to a substrate a coating composition comprising a radiation curable resin binder whose curing is inhibited by oxygen, a non-volatile photoinitiator, and a flow control agent;

in a first exposure step exposing the coating in the presence of oxygen to ionizing radiation so as to at least partially cure a subsurface layer of the coating while leaving an at least partially uncured surface layer; in a subsequent exposure step exposing the coating in a substantially inert atmosphere to ultraviolet radiation sufficient to cure the surface of the coating to produce high gloss surface.

13. The method of claim 12 wherein the photoinitiator is characterized by a molecular weight of at least 260.

14. The method of claim 12 wherein the photoinitiator is characterized by a molecular weight of at least 300.

15. The method of claim 12 wherein the photoinitiator is characterized by a molecular weight of at least 1000.

16. The method of claim 12 wherein the photoinitiator is characterized by a functional group copolymerizable with other polymerizable constituents of the composition.

17. The method of claim 12 wherein the photoinitiator comprises a substituted acetophenone derivative.

18. The method of claim 12 wherein the flow control agent is selected from the group consisting of silanes and fluorocarbons.

19. The composition of claim 18 wherein the flow control agent is a polysiloxane.

20. The method of claim 12 wherein the coating composition comprises:

10-99 weight percent of the binder;

0.01-4 weight percent of the photoinitiator; and

0.01-1 weight percent of the flow control agent.

21. The method of claim 1s wherein at least 10 percent by weight of the binder is polyacrylyloxy compound.

22. The method of claim 12 wherein at least 30 percent by weight of the binder is polyacrylyloxy compound.

23. The method of claim 12 wherein said ionizing radiation step is carried out in an atmosphere containing greater than 200 parts per million of oxygen.

24. The method of claim 12 wherein said ionizing radiation step is carried out in an atmosphere containing greater than 1000 parts per million of oxygen.

25. The method of claim 12 wherein said ultraviolet exposure step is carried out in an atmosphere containing less than 1000 parts per million of oxygen.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/02939

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B05D3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 B05D C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 309 452 (SACHS) 5 January 1982 see the whole document ---	12,21, 23-25
X	US,A,4 326 001 (SACHS ET AL.) 20 April 1982 see the whole document ---	12,21, 23-25
X	US,A,4 048 036 (PRUCNAL) 13 September 1977 cited in the application see the whole document ---	1-5
X	EP,A,0 352 821 (NIPPONDENSO CO. LTD. ET AL.) 31 January 1990 see the whole document ---	1-6,9
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
10 August 1994	02.09.94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Brothier, J-A

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/02939

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US,A,4 999 136 (SU ET AL.) 12 March 1991 see the whole document	1-7,9,10
A	US,A,4 428 974 (OKITA ET AL.) 31 January 1984 see the whole document	12

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